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## (54) METHOD OF PRODUCTION OF GRANULAR TANTALUM OXIDE OR NIOBIUM OXIDE

## (57) [ABSTRACT]

[CONFIGURATION] A method of production of granular tantalum oxide or niobium oxide comprising the steps of adding ammonia to a solution of tantalum fluoride or niobium fluoride to precipitate tantalum hydroxide or niobium hydroxide, washing the precipitate, then firing the same, the method of production of granular tantalum oxide or niobium oxide controlling the particle size, BET, and fluorine content of the granular tantalum oxide or niobium oxide by washing the precipitate until the fluorine concentration in a filtered liquid after the washing becomes a predetermined range.

[EFFECT] By checking the fluorine concentration in the filtered liquid after the washing, the tantalum oxide or the niobium oxide having a desired particle size, fluorine content, and BET can be obtained.

## [CLAIMS]

[Claim 1] A method of production of granular tantalum oxide or niobium oxide comprising steps of adding ammonia to a solution of tantalum fluoride or niobium fluoride to precipitate tantalum hydroxide or niobium hydroxide, washing the precipitate, and then firing the same, the method of production of granular tantalum oxide or niobium oxide characterized by controlling the particle size, BET, and fluorine content of the granular tantalum oxide or niobium oxide by washing the precipitate until the fluorine concentration in a filtered liquid after the washing becomes a predetermined range.

## [DETAILED DESCRIPTION OF THE INVENTION]

## [0001]

[Field of Utilization in Industry] The present invention relates to a method of production of tantalum oxide or niobium oxide used in the ceramic field, single crystal field, optical glass field, etc., in more detail, relates to a method of production of tantalum oxide or niobium oxide having a predetermined particle size, BET, and fluorine content.

## [0002]

[Prior Art] Conventionally, as the method of production of tantalum oxide or niobium oxide, a method of production of tantalum oxide or niobium oxide comprising the steps of incorporating ammonia, ammonium carbonate, ammonium bicarbonate, or an alkali containing CO<sub>2</sub>, into a solution of a tantalum compound or a niobium compound to precipitate tantalum hydroxide or niobium hydroxide and firing the precipitate is well known (for example, Japanese Patent Publication (B) No. 49-30354, Japanese Patent Publication (A) No. 51-10197, Japanese Patent Publication (A) No. 1-115820, and Japanese Patent Publication (A) No. 1-176226).

[0003] When generating a precipitate of tantalum hydroxide or niobium hydroxide using ammonium bicarbonate, in general, the particles of the precipitate (primary particles) become large. When firing them, the primary particles

agglomerate (abnormal growth of particles is caused) to generate further larger secondary particles. Even if these secondary particles are broken down (not pulverized), the BET of the generated oxide after the breakdown is 0.2 to 0.5 m<sup>2</sup>/g, and the grain becomes only 7 to 20 μm. On the other hand, when generating a precipitate by using ammonia, in general, the BET of the generated oxide after the firing and the breakdown becomes only 2 to 3 m<sup>2</sup>/g, and the grain becomes only 7 to 10 μm.

[0004]

[Problem to be Solved by Invention] Naturally, a smaller amount of the remaining fluorine in the generated tantalum oxide or niobium oxide is preferred, but the user of the tantalum oxide or the niobium oxide requires materials having good reactivity with respect to various types of reactions and good dispersion property in a liquid, and having better dielectric characteristic where used in a dielectric body. From such requests, granular tantalum oxide or niobium oxide having a small particle size and having a BET as large as possible is demanded. Further, naturally particles that cause abnormal firing at the time of firing is not preferred. Further, when taking this into account from the viewpoint of the material cost, use of an ammonium carbonate series is more advantageous than use of the ammonia.

[0005]

The present invention was made in consideration with such problems of the prior art. An object of the present invention is to provide a method of production of tantalum oxide or niobium oxide having little remaining fluorine, having a small particle size, and having a BET as large as possible and having a predetermined particle size, BET, and fluorine content.

[0006]

[Means for Solving the Problem] The present inventors engaged in repeated studies for solving the above problems and consequently found the facts that there is a correlation between the fluorine concentration in the washed precipitate

when washing the tantalum hydroxide or niobium hydroxide precipitate obtained by adding ammonia to a solution of tantalum fluoride or niobium fluoride (organic acid solution such as fluoric acid or oxalic acid) and the fluorine concentration in the filtered liquid after the washing, that the lower the F concentration in the obtained tantalum hydroxide or niobium hydroxide precipitate, the easier the caking occurring in the drying and firing, and that, therefore, when the F concentration was relatively high, the caking was eased in the drying and firing and that accordingly the primary particle size of the precipitate, the particle size of the generated tantalum oxide or niobium oxide, and the BET can be controlled by adjusting the fluorine concentration in the generated hydroxide by washing the precipitate until the fluorine concentration in the filtered liquid after the washing became the predetermined range and thereby reached the present invention.

[0007] Namely, in the method of production of granular tantalum oxide or niobium oxide comprising the steps of adding ammonia to a solution of tantalum fluoride or niobium fluoride to precipitate tantalum hydroxide or niobium hydroxide, washing the precipitate, then firing the same, the method of production of granular tantalum oxide or niobium oxide of the present invention characterized in that the particle size, BET, and fluorine content of the granular tantalum oxide or niobium oxide are controlled by washing the precipitate until the fluorine concentration in the filtered liquid after washing becomes a predetermined range.

[0008] By adding ammonia to a solution of tantalum fluoride or niobium fluoride to precipitate tantalum hydroxide or niobium hydroxide and washing the precipitate, the fluorine concentration in the precipitate is reduced. According to many experiments conducted by the present inventors, it was found that there is a correlation between the fluorine concentration in the washed precipitate when washing tantalum hydroxide or niobium hydroxide precipitate obtained by adding ammonia to the solution of tantalum

fluoride or niobium fluoride and the fluorine concentration in the filtered liquid after washing. The measurement of the fluorine concentration in the precipitate generally takes a long time, so it is difficult to apply this to a production process. However, measurement of the fluorine concentration in a liquid is easy. Accordingly, it is convenient for application to a production process to estimate the fluorine concentration in the precipitate by measuring the fluorine concentration in the filtered liquid after washing.

[0009] Further, it was found from many experiments conducted by the present inventors that the fluorine in the precipitate promoted or suppressed the sintering at the time of firing, therefore, by adjusting the fluorine concentration in the generated hydroxide, the abnormal growth of particles at the time of firing after that can be prevented and the particle size of the generated tantalum oxide or niobium oxide can be controlled.

[0010] Below, the present invention and effects thereof will be explained in further detail based on examples.

[0011]

[Examples]

Example 1

Ammonia water was added into a fluoric acid solution of niobium to generate a precipitate of niobium hydroxide. This precipitate was divided into small groups which were washed to various extents and filtered. The fluorine concentration in the filtered liquid after the washing (measured value by an ion meter), the fluorine concentration in the niobium hydroxide, and the BET of the niobium hydroxide particles after drying the filtered remainder at 130°C were as shown in Table 1. The fluorine concentration in the niobium oxide obtained by firing the niobium hydroxide at 765°C and breaking down the same and the BET, brain (mean particle size of all particles measured by the air permeation method),  $D_{50}$  (particle size corresponding to 50% of the particle size distribution, value by micro track method), and amount of +325M (remainder on 325 mesh wet type comb after dispersing

it for 1 minute by ultrasonic wave) of the niobium oxide particles were as shown in Table 1.

[0012]

[Table 1]

Washing times	F concen-tration of filtered liquid ppm	Precipitate		Generated oxide				
		F con-cen-tration ppm	BET m <sup>2</sup> /g	F con-cen-tration ppm	BET m <sup>2</sup> /g	Brain μm	D <sub>50</sub> μm	+325M %
0 time	19200	9.9	9.2	130	6.9	0.74	1.10	19.26
1 time	7700	6.6	67	60	9.2	0.53	1.04	2.58
2 times	4200	2.8	90	30	9.8	0.46	0.61	0.10
3 times	2900	0.91	00	<1	9.3	0.48	0.86	0.47
4 times	1750	0.39	04	<1	9.1	0.48	0.95	0.08
5 times	1350	1.1	93	<1	8.4	0.50	0.96	0.37
6 times	970	0.75	98	<1	7.5	0.52	0.96	0.07
7 times	540	0.45	15	<1	6.9	0.56	1.01	0.34
8 times	300	0.09	14	<1	6.2	0.61	1.01	4.49
9 times	230	0.13	03	<1	6.1	0.64	1.01	7.81

[0013] As apparent from the data of Table 1, in the method of production of niobium oxide by adding ammonia to a fluoric acid solution of niobium to precipitate niobium hydroxide, washing the precipitate, then firing and breaking down the same, by performing the washing until the fluorine concentration in the filtered liquid after the washing becomes about 3000 ppm or less (that is, until the fluorine concentration in the precipitate becomes 0.9% or less), the fluorine concentration in the generated oxide after the firing can be controlled to 10 ppm or less and further 1 ppm or less and by performing the washing to an extent such that the fluorine concentration in the filtered liquid after the washing is 500 ppm or more (that is, an extent where the fluorine concentration in the precipitate is 0.2% or more), the abnormal growth of the particles of the generated oxide after the firing can be prevented. Conversely, by performing the washing until the fluorine concentration in the filtered liquid after washing becomes 400 ppm or less (that is, until the fluorine concentration in the precipitate becomes 0.2% or less), it is also possible to produce the sintered particles at the time of firing.

[0014] When showing the relationship between the fluorine concentration in the filtered liquid after the

washing and the fluorine concentration in the washed precipitate in the graph from the data of Table 1, the result becomes as shown in FIG. 1. As apparent also from FIG. 1, the fluorine concentration in the filtered liquid after the washing and the fluorine concentration in the washed precipitate have a clear correlation. Accordingly, by measuring the fluorine concentration in the filtered liquid after the washing, the fluorine concentration in the washed precipitate can be clearly estimated. When showing the relationship between the fluorine concentration in the filtered liquid after the washing and the BET of the oxide after firing in the graph, the result becomes as shown in FIG. 2. As apparent also from FIG. 2, by performing the washing until the fluorine concentration in the filtered liquid after the washing becomes a range of from 2000 to 10000 ppm, the BET of the oxide after the firing can be made large. When showing the relationships between the fluorine concentration in the filtered liquid after the washing and the brain, micro track  $D_{50}$ , and +325M of the oxide after the firing in the graphs, the results become as shown in FIG. 3, FIG. 4, and FIG. 5. As apparent also from FIG. 3 to FIG. 5, particularly FIG. 5, by performing the washing until the fluorine concentration in the filtered liquid after the washing becomes a range of from 500 to 3000 ppm (that is, until the fluorine concentration in the precipitate becomes a range of from 0.2 to 0.9%), the particle size of the oxide after the firing can be controlled, and 99.5% or more of the oxide can be made -325 mesh.

[0015] Example 2

Ammonia water was added to a fluoric acid solution of tantalum to generate a precipitate of tantalum hydroxide. This precipitate was divided into small groups which were then washed to various extents and filtered. The fluorine concentration in the filtered liquid after the washing and the fluorine concentration in the tantalum hydroxide after drying the filtration remainder at 130°C were as shown in Table 1. The fluorine concentration in the tantalum oxide

obtained by firing these tantalum hydroxides at 1000°C and breaking down the same, and the BET, brain,  $D_{50}$ ,  $D_{90}$ , and amount of +325M thereof were as shown in Table 2.

[0016]

[Table 2]

Washing times	F concen-tration of filtered liquid ppm	F concen-tration of precipitate	Generated Oxide						+325M %
			F concen-tration ppm	BET m <sup>2</sup> /g	Brain μm	$D_{50}$ μm	$D_{90}$ μm		
0 time	19500	11.7	3900	5.23	0.93	1.50	3.61		31.0
1 time	6500	5.6	2700	2.83	0.71	1.25	2.96		1.0
2 times	4100	3.3	980	2.95	0.62	0.95	2.35		25.8
3 times	2700	1.7	450	3.72	0.69	0.89	2.13		37.5
4 times	1100	0.75	180	4.00	0.72	0.86	2.05		40.3
5 times	440	0.24	40	4.03	0.61	0.93	2.28		34.4
6 times	170	0.06	10	4.02	0.64	0.93	2.22		39.3

[0017] When showing the relationship between the fluorine concentration in the filtered liquid after the washing and the fluorine concentration in the washed precipitate in the graph from the data of Table 2, the result becomes as shown in FIG. 6. As apparent also from FIG. 6, the fluorine concentration in the filtered liquid after the washing and the fluorine concentration in the washed precipitate have a clear correlation. Accordingly, by measuring the fluorine concentration in the filtered liquid after the washing, the fluorine concentration in the washed precipitate can be clearly estimated. When showing the relationship between the fluorine concentration in the filtered liquid after the washing and the BET of the oxide after the firing in the graph, the result becomes as shown in FIG. 7. When showing the relationships between the fluorine concentration in the filtered liquid after the washing and the brain, the micro track,  $D_{50}$ , and +325M of the oxide after the firing in graphs, they become as shown in FIG. 8, FIG. 9, and FIG. 10. As apparent also from FIG. 8 to FIG. 10, by performing the washing until the fluorine concentration in the filtered liquid after the washing becomes the range of from 500 to 3000 ppm, the particle size of the oxide after the firing can be controlled small.

[0018]

[Effect of the Invention] By checking the fluorine concentration in the filtered liquid after the washing in the method of production of the present invention, tantalum oxide or niobium oxide having desired particle size, fluorine content, and BET can be obtained.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1] A graph showing the relationship between the fluorine concentration in a filtered liquid after washing and the fluorine concentration in a washed precipitate.

[FIG. 2] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and BET of an oxide after firing.

[FIG. 3] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and brain of the oxide after the firing.

[FIG. 4] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and micro track  $D_{50}$  of the oxide after the firing.

[FIG. 5] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and +325M of the oxide after the firing.

[FIG. 6] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and the fluorine concentration in the washed precipitate.

[FIG. 7] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and BET of the oxide after the firing.

[FIG. 8] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and brain of the oxide after the firing.

[FIG. 9] A graph showing the relationship between the fluorine concentration in the filtered liquid after the washing and micro track  $D_{50}$  of the oxide after the firing.

[FIG. 10] A graph showing the relationship between the fluorine concentration in the filtered liquid after the

washing and +325M of the oxide after the firing.

[FIG. 1]

F CONCENTRATION IN PRECIPITATE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 2]

BET OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 3]

BRAIN OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 4]

MICRO TRACK  $D_{50}$  OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 5]

AMOUNT OF +325M OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 6]

AMOUNT OF +325M OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 7]

MICRO TRACK  $D_{50}$  OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 8]

BRAIN OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 9]

BET OF OXIDE

F CONCENTRATION IN FILTERED LIQUID

[FIG. 10]

F CONCENTRATION IN PRECIPITATE

F CONCENTRATION IN FILTERED LIQUID

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